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A note concerning second and third order optical and magneto-optical activity

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Recently the optical rotatory dispersion (ORD) and circular dichroism (CD) and their magnetic analogues—the magneto-optical rotatory dispersion (MORD) and magnetic circular dichroism (MCD) have received considerable interest in spectral investigations of molecular structure (Buckingham & Stephens 1966). For light of very high intensity, *e g.* a laser beam, the molecular response to the light is nonlinear and this gives rise to multiphoton absorption and harmonic generation (Armstrong *et al* 1962). We have looked into the significance of bi-photonic absorption and second harmonic generation in relation to optical and magneto-optical rotations, and have derived expressions for the latter.

We have used the formalism of quantized field and have decomposed the electric and the magnetic field vector of the light in terms of Fourier components and Creation and Annihilation operators (Heitler 1953) The expressions for rotation of the plane of polarization of the incident light and its ellipticity are obtained as the expectation values of the corresponding Stokes operators (Jauch & Rohrlich 1955). In our description of the near-resonance processes, the generalised perturbation theory of Heitler & Ma (1949) revived by Hameka (1962) was used. The process of second harmonic generation does not conserve the total number of photons, and therefore, we have resorted to an oscillatory coherent wave-packet description of the incident light.

Our main conclusions are as follows :

1) The optical and magneto-optical rotations should show a dispersion anomaly at the second harmonic frequency corresponding to the biphotonic absorption band.

The general expression for the complex rotation is given by

$$\hat{\phi}_{non-linear} = \frac{8\pi^2 I\omega N}{\hbar^3 c} \sum_{l,l',m} Av\, \frac{\omega(2\omega^2+2\omega_l\omega_{l'}+\omega_l\omega_m+\omega_{l'}\omega_m) Im(\widetilde{D}_{ll'm}+\widetilde{M}_{ll'm})}{(\omega^2-\omega_l^2+i\omega_l\gamma_l)(\omega^2-\omega_{l'}^2+i\omega_l\gamma_{l'})}$$

$$\frac{-i(\omega_m\omega^2+\omega_m\omega_l\omega_{l'}+2\omega^2\omega_l+2\omega^2\omega_{l'}) Re(\widetilde{D}_{ll'm}+\widetilde{M}_{ll'm})}{(4\omega^2-\omega_m^2+2i\omega_m\gamma_m)}$$

Here I is the intensity of the incident light beam of frequency ω; ω_l, $\omega_{l'}$ and ω_m are excitation energies for states l, l' and m, respectively; γ_l, $\gamma_{l'}$ and γ_m are the corresponding band-widths; and Av denotes averaging with respect to molecular orientations. The matrix elements $\widetilde{D}_{ll'm}$ and $\widetilde{M}_{ll'm}$ are given by

$$\widetilde{D}_{ll'm} = D_{yxx\lambda} + D_{xyxx}$$

$$\widetilde{M}_{ll'm} = M_{\bar{y}yxx} + M_{xy\bar{y}x} + M_{xyx\bar{y}} + M_{y\bar{y}xx} - M_{\bar{x}xxx} - M_{x\bar{x}xx}$$

where

$D_{\alpha\beta\gamma\delta}$ and $M_{\alpha\beta\gamma\delta}$ are the abbreviations of

$<a|D_\alpha|l><l|D_\beta|m><m|D_\gamma|l'><l'|D_\delta|a>$ and

$<a|M_\alpha|l><l|D_\beta|m><m|D_\gamma|l'><l'|D_\delta|a>$ respectively.

Quantities like D_α and M_α denote the component of electric and magnetic dipole operators, respectively, and $|a>$ the ground state of the molecules.

(2) The third order optical birefringence is observable only for molecules lacking planes of reflection symmetry, and third order optical rotation is observable only for molecules lacking planes of reflection symmetry and/or inversion symmetry—the requirements being the same as those for linear birefringence and optical activity, respectively. These follow from the symmetries of matrix-elements $\widetilde{D}_{ll'm}$ and $\widetilde{M}_{ll'm}$

(3) If an intense polarized light beam, containing a small amount of coherently matched similarly polarised second harmonic, is allowed to pass through a substance along or perpendicular to the direction of the magnetic field, a magneto-optical rotation of the second harmonic may occur due to the production of a second harmonic polarised perpendicular to the incident beam

(4) An optical rotation of a generated second harmonic should occur for a set-up as in (3) in the absence of a magnetic field for crystals lacking centre of inversion symmetry, the conditions being the same as those for second harmonic generation.

(5) The above non-linear effects will be observable at high photon densities ($\simeq 10^{23}$) achievable with laser source.

The dispersion curves for the above non-linear processes contain contribution from states which are ordinarily inaccessible due to the forbiddenness of the ordinary transitions In addition, the high-lying exicited states might be located by observing the dispersion anomaly of the inducing light due to third order optical and Faraday rotation. The linear dispersion anomaly in this case may be very difficult to observe because of technical difficulties to be faced at short wave lengths.

The details of the derivation and expressions for the above-mentioned non-linear effects will be published soon

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